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<p>(54) Title: METHOD FOR SPRAY TANK CLEANOUT</p> <p>(57) Abstract</p> <p>A method for facilitating cleanout of residual sulfonylurea pesticide from spray tank equipment comprising (i) formulating the sulfonylurea as an agriculturally suitable water-soluble salt composition before spray tank application, (ii) applying the salt composition to the crop and (iii) rinsing the tank substantially free of residual sulfonylurea more easily than is possible when the sulfonylurea is not formulated as a salt.</p>		

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TITLE

METHOD FOR SPRAY TANK CLEANOUT

Sulfonylureas, as a class, are highly active
5 pesticides. For this reason, care must be taken to
make sure that all traces of sulfonylurea are cleaned
out of the spray equipment (hereafter referred to as
spray tank), which is used to apply pesticides to
crops, before an applicator uses this equipment in a
10 subsequent application to treat a crop that is
sensitive or will be injured by the sulfonylurea used
in the previous spray tank application. Adequate
cleanout may require a rinsing procedure that is time-
consuming and causes an environmental waste-water
15 disposal problem.

Salts of the sulfonylureas are generally known as
are methods for making them. What has not been
appreciated until now is the advantage that can be
achieved in spray tank cleanout when the sulfonylurea
20 active ingredient is applied in its salt form rather
than in its acid form. The described salt formulations
can be applied conventionally or using chemical
injection technology since the soluble formulation
gives a solution that can be uniformly injected into
25 the spray boom.

SUMMARY OF THE INVENTION

This invention concerns a method for reducing
residual sulfonylurea pesticide contamination of a
spray tank from which the sulfonylurea is applied,
30 comprising the steps:

i) formulating the sulfonylurea active
ingredient as an agriculturally suitable water soluble
salt composition before spray tank application, thereby
increasing solubility of the sulfonylurea and

decreasing the amount of insoluble sulfonylurea available for residual contamination of the spray tank,

ii) applying the sulfonylurea salt composition to the crop while minimizing buildup of insoluble
5 sulfonylurea in the spray tank, and

iii) rinsing the spray tank substantially free of residual sulfonylurea, after application, in an operation in which the sulfonylurea remaining in the spray tank is reduced significantly versus the amount
10 remaining when sulfonylurea is not formulated as a water-soluble salt before application.

The sulfonylureas whose spray tank buildup is curtailed by the method of this invention are the sulfonylurea acids either when used alone or with one
15 or more tank mix partners. The benefits achieved by this invention have been found to be more pronounced when the sulfonylurea is employed with a tank mix partner. The benefits are even more noteworthy when earlier tank mixes have left organic deposits on inside
20 spray tank surfaces. In such instances, it is believed that undissolved particles of the sulfonylurea are held by the organic deposit and kept from becoming resuspended or dissolved in the spray tank water. Thereafter, should the spray tank be employed on a crop
25 sensitive to the sulfonylurea, damage may result either from migration into the tank water of particles formerly trapped by the organic deposit or by actual sloughing off of the organic deposit carrying embedded sulfonylurea particles with it.

30 The problem of difficult spray tank cleanout is exacerbated by sulfonylureas used at relatively high concentrations. Since water solubility of the sulfonylurea active ingredient in its acid form is so low, tank mixes of the sulfonylureas are primarily
35 suspensions. Suspended particles can collect on tank

walls, in tubing, or be trapped by organic deposits that may be present inside the tank. If a later tank mix sends the sulfonylurea into solution or suspension, sensitive crops can be damaged.

5 This problem is avoided by employing sulfonylureas in a water-soluble form. The sulfonylurea salt form shows a faster dissolution rate than the corresponding sulfonylurea acid, particularly evident at low pH's. Thus, at typical use rates, there will be little or no
10 sulfonylurea particles to build up on interior tank surfaces or become imbedded in organic deposits that may have formed on such surfaces. Use of sulfonylureas in their salt form rather than their acid form has been found, under a variety of circumstances, to result in a
15 greater than fourfold improvement in spray tank cleanout.

 Preferred salt cations (M) are the sodium, potassium, calcium, magnesium, ammonium and alkylammonium cations. Preferred sulfonylurea salts
20 are the sodium and calcium salts of tribenuron methyl, the potassium salt of thifensulfuron methyl, the ammonium salt of chlorsulfuron and the potassium salt of metsulfuron methyl.

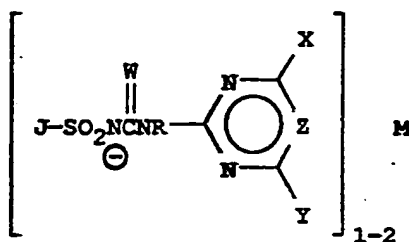
BRIEF DESCRIPTION OF THE DRAWINGS

25 The Figures represent comparisons in bar graph format of the data summarized in the Tables. Figure 1 shows a statistically significant distinction between ease of cleanout of sulfonylurea-tank partner mixtures (37% failure rate) vs. cleanout of corresponding
30 sulfonylurea salt-tank partner mixtures (8% failure). Figure 2 shows an even greater distinction when no tank partners are present (89% failure for sulfonylurea acid and 11% failure for the salt formulation).

DETAILS OF THE INVENTION

Representative of the sulfonylureas whose salt forms are contemplated for use in the process of this invention are those of the formula:

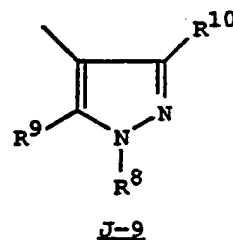
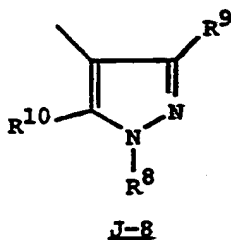
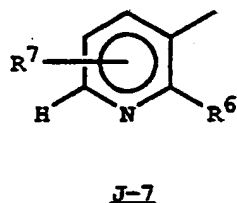
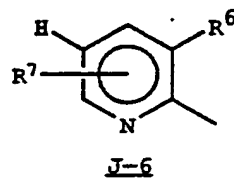
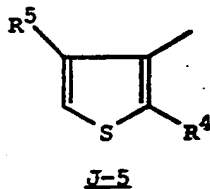
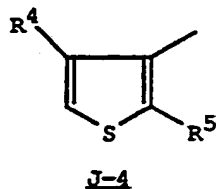
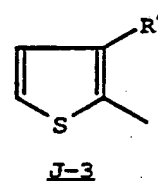
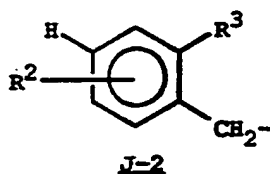
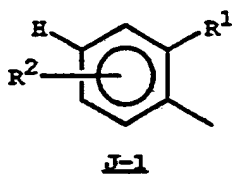
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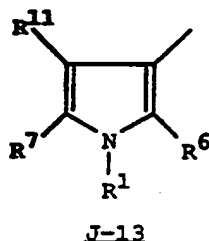
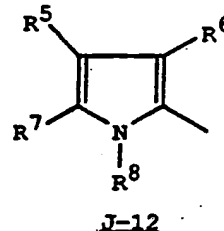
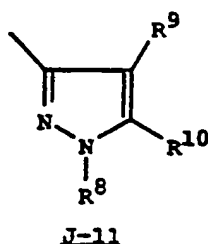
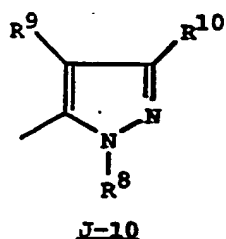
wherein:

J is selected from the group

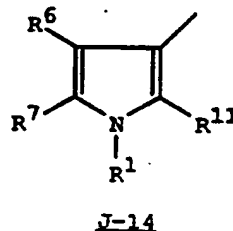
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5



and



R is selected from the group H and CH₃;

R¹ is selected from the group F, Cl, Br, NO₂, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₃-C₄ cycloalkyl, C₂-C₄ haloalkenyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, C₂-C₄ alkoxyalkoxy, CO₂R¹², C(O)NR¹³R¹⁴, SO₂NR¹⁵R¹⁶, S(O)_nR¹⁷, C(O)R¹⁸, CH₂CN and L;

R² is selected from the group H, F, Cl, Br, CN, CH₃, OCH₃, SCH₃, CF₃ and OCF₂H;

R³ is selected from the group Cl, NO₂, CO₂CH₃, CO₂CH₂CH₃, SO₂N(CH₃)₂, SO₂CH₃, SO₂CH₂CH₃, OCH₃, and OCH₂CH₃;

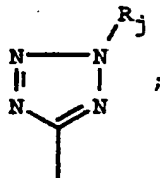
R⁴ is selected from the group C₁-C₃ alkyl, C₁-C₂ haloalkyl, C₁-C₂ alkoxy, C₂-C₄ haloalkenyl, F, Cl, Br, NO₂, CO₂R¹², C(O)NR¹³R¹⁴, SO₂NR¹⁵R¹⁶, S(O)_nR¹⁷, C(O)R¹⁸ and L;

R⁵ is selected from the group H, F, Cl, Br and CH₃;

R⁶ is selected from the group C₁-C₃ alkyl, C₁-C₂ alkoxy, C₂-C₄ haloalkenyl, F, Cl, Br, CO₂R¹², C(O)NR¹³R¹⁴, SO₂NR¹⁵R¹⁶, S(O)_nR¹⁷, C(O)R¹⁸ and L;

R⁷ is selected from the group H, F, Cl, CH₃ and CF₃;

- R^8 is selected from the group H, C_1-C_3 alkyl and pyridyl;
- R^9 is selected from the group C_1-C_3 alkyl, C_1-C_2 alkoxy, F, Cl, Br, NO_2 , CO_2R^{12} , $SO_2NR^{15}R^{16}$, $S(O)_nR^{17}$, OCF_2H , $C(O)R^{18}$, C_2-C_4 haloalkenyl and L;
- R^{10} is selected from the group H, Cl, F, Br, C_1-C_3 alkyl and C_1-C_2 alkoxy;
- R^{11} is selected from the group H, C_1-C_3 alkyl, C_1-C_2 alkoxy, C_2-C_4 haloalkenyl, F, Cl, Br, CO_2R^{12} , $C(O)NR^{13}R^{14}$, $SO_2NR^{15}R^{16}$, $S(O)_nR^{17}$, $C(O)R^{18}$ and L;
- R^{12} is selected from the group allyl and propargyl and C_1-C_3 alkyl optionally substituted by at least one member independently selected from halogen, C_1-C_2 alkoxy and CN;
- R^{13} is selected from the group H, C_1-C_3 alkyl and C_1-C_2 alkoxy;
- R^{14} is C_1-C_2 alkyl;
- R^{15} is selected from the group H, C_1-C_3 alkyl, C_1-C_2 alkoxy, allyl and cyclopropyl;
- R^{16} is selected from the group H and C_1-C_3 alkyl;
- R^{17} is selected from the group C_1-C_3 alkyl, C_1-C_3 haloalkyl, allyl and propargyl;
- R^{18} is selected from the group C_1-C_4 alkyl, C_1-C_4 haloalkyl and C_3-C_5 cycloalkyl optionally substituted by halogen;
- n is 0, 1 or 2;
- M is a cation;
- L is



R_j is selected from the group H and C₁-C₃ alkyl;

W is selected from the group O and S;

X is selected from the group H, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, C₁-C₄ haloalkyl, C₁-C₄ haloalkylthio, C₁-C₄ alkylthio, halogen, C₂-C₅ alkoxyalkyl, C₂-C₅ alkoxyalkoxy, amino, C₁-C₃ alkylamino and di(C₁-C₃ alkyl)amino;

Y is selected from the group H, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, C₁-C₄ alkylthio, C₁-C₄ haloalkylthio, C₂-C₅ alkoxyalkyl, C₂-C₅ alkoxyalkoxy, amino, C₁-C₃ alkylamino, di(C₁-C₃ alkyl)amino, C₃-C₄ alkenyloxy, C₃-C₄ alkynyloxy, C₂-C₅ alkylthioalkyl, C₂-C₅ alkylsulfinylalkyl, C₂-C₅ alkylsulfonylalkyl, C₁-C₄ haloalkyl, C₂-C₄ alkynyl, C₃-C₅ cycloalkyl, azido and cyano;

Z is selected from the group CH and N;

provided that i) when one or both of X and Y is C₁ haloalkoxy, then Z is CH; and ii) when X is halogen, then Z is CH and Y is OCH₃, OCH₂CH₃, N(OCH₃)CH₃, NHCH₃, N(CH₃)₂ or OCF₂H.

Salts of the following sulfonylureas are preferred for use in the disclosed process: 2-chloro-N-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]-benzenesulfonamide (chlorsulfuron); methyl 2-[[[(4,6-dimethyl-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-benzoate (sulfometuron methyl); ethyl 2-[[[(4-chloro-6-methoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-benzoate (chlorimuron ethyl); methyl 2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoate (metsulfuron methyl); methyl 2-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-6-(trifluoromethyl)-3-pyridine-carboxylate; methyl 2-[[[(4-ethoxy-6-(methylamino)-1,3,5-triazin-2-

yl]amino]carbonyl]amino]sulfonyl]benzoate
 (ethametsulfuron methyl); 2-(2-chloroethoxy)-N-[[[(4-
 methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]-
 benzenesulfonamide; ethyl 5-[[[(4,6-dimethoxy-2-
 5 pyrimidinyl)amino]carbonyl]amino]sulfonyl]-1-methyl-1H-
 pyrazole-4-carboxylate; N-[[[(4,6-dimethoxy-2-
 pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2-
 pyridinesulfonamide (rimsulfuron); methyl 3-[[[(4-
 methoxy-6-methyl-1,3,5-triazin-2-
 10 yl)amino]carbonyl]amino]sulfonyl]-2-
 thiophenecarboxylate (thifensulfuron methyl); methyl 2-
 [[[[N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-N-
 methylamino]carbonyl]amino]sulfonyl]benzoate
 (tribenuron methyl); methyl 2-[[[[[(4,6-dimethoxy-2-
 15 pyrimidinyl)amino]carbonyl]amino]-
 sulfonyl]methyl]benzoate (bensulfuron methyl);
 2-[[[[[(4,6-dimethoxy-2-
 pyrimidinyl)amino]carbonyl]amino]sulfonyl]-N,N-
 dimethyl-3-pyridinecarboxamide (nicosulfuron); methyl
 20 2-[[[[[(4,6-bis(difluoro-methoxy)-2-pyrimidinyl)amino]-
 carbonyl]amino]sulfonyl]benzoate; methyl 2-[[[[[(4-
 dimethylamino)-6-(2,2,2-trifluoroethoxy)-1,3,5-triazin-
 2-yl]amino]carbonyl]amino]sulfonyl]-3-methylbenzoate;
 and N-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-1-
 25 methyl-4-(2-methyl-2H-tetrazol-5-yl)-1H-pyrazole-5-
 sulfonamide.

More preferred are sulfonylurea salts of the
 following sulfonylureas: 3-[[[[[(4-methoxy-6-methyl-
 1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-
 30 thiophenecarboxylate (thifensulfuron methyl), methyl 2-
 [[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]-
 carbonyl]amino]sulfonyl]benzoate (metsulfuron methyl),
 methyl 2-[[[[N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-
 N-methylamino]carbonyl]amino]sulfonyl]benzoate
 35 (tribenuron methyl) and 2-chloro-N-[[[(4-methoxy-6-

methy1-1,3,5-triazin-2-yl)amino]carbonyl]benzene-sulfonamide (chlorsulfuron) wherein M is selected from the group sodium, potassium, calcium, ammonium, and alkylammonium.

- 5 Sulfonylurea salts of this invention can be used alone or in combination with other commercial herbicides (including other sulfonylureas or sulfonylurea salts), insecticides or fungicides. Mixtures containing sulfonylurea salts are particularly
10 useful in minimizing spray tank cleanout when compared to the same mixtures containing the corresponding sulfonylurea acid.

- The data summarized in Table I (using Protocol I) show that the sulfonylurea acid plus tank mix partner
15 suffered a failure rate of 37% (10 failures out of 27) whereas the corresponding alkali metal salt of the sulfonylurea plus tank mix partner had a failure rate of only about 8% (2 failures out of 24). (NOTE: Test failure corresponds to a greenhouse result of >20%
20 injury to sugarbeets in the bioassay test.) The data summarized in Table II (using Protocol II) show that in the absence of a tank partner, cleanout of the sulfonylurea salt formulation is equivalent to or more effective than cleanout of the corresponding
25 sulfonylurea acid. The corresponding tank cleanout Protocols I and II are described after each table, followed by the bioassay protocol. Each of the percent injury figures in the tables is the average of two bioassay results of the two samples of the final
30 ammonia wash water: one sample taken from the tank and one sample taken from the boom.

TABLE I
Sprayer Cleanout
Sulfonylurea Plus Tank Mix Partner

<u>Sulfonylurea</u>	<u>Initial Sulfonylurea Concentration in the Tank Mix (ppm)</u>	<u>Tank Mix Partner</u>	<u>Percent Injury¹</u>
Thifensulfuron methyl	400	2,4-D	60
	400	MCPA	100
	500	propiconazole	90
Thifensulfuron methyl + Metsulfuron methyl (10:1)	190	propiconazole	0
	380	propiconazole	100
	600	propiconazole	0
	600	propiconazole	20
	600	propiconazole	0
	600	flutriafol	70
	600	flutriafol	20
Thifensulfuron + Tribenuron methyl (2:1)	600	2,4-D	0
	600	2,4-D	0
	600	2,4-D	0
	600	2,4-D	60
	775	2,4-D	0
	1000	2,4-D	0
	530	2,4-D/surfactant	0
	450	MCPA	50
	430	MCPA	0
	750	MCPA	10
	750	MCPA	0
	1070	MCPA	0
	835	propiconazole	100
Tribenuron methyl	149	propiconazole	50
	168	propiconazole	0
	200	propiconazole	0
	200	propiconazole	90

Potassium Salt of	232	propiconazole	0
Thifensulfuron methyl	400	propiconazole	0
	500	propiconazole	90
	400	2,4-D	0
	407	flutriafol	0
	570	flutriafol	20
Potassium Salt of	660	propiconazole	30
Thifensulfuron methyl	660	propiconazole	0
+ Metsulfuron			
methyl (10:1)			
Potassium Salt of	700	2,4-D	0
Thifensulfuron methyl	700	2,4-D	0
+ Sodium Salt of	1150	2,4-D	5
Tribenuron	1150	2,4-D	0
methyl (2:1)	130	MCPA	2
	675	MCPA	2
	700	MCPA	0
	720	MCPA	0
	700	propiconazole	0
	770	propiconazole	0
Sodium Salt of	117	2,4-D	0
Tribenuron	200	propiconazole	0
methyl	224	propiconazole	0
	246	propiconazole	2
	268	propiconazole	0
	281	propiconazole	0

¹Percent injury to greenhouse sugarbeets after sprayed with final ammonia wash water from the tank cleanout procedure.

TANK CLEANOUT PROTOCOL I
(Sulfonylurea Plus Tank Mix Partner)

Step 1

- 5 Add water to the tank and when half-filled, add the sulfonylurea or the sulfonylurea salt with agitation. Fill tank to the 90% level with water, add any tank mix partners, and finish filling the tank. Agitate the tank mix for a minimum of 5 to 10 minutes.

Step 2

- 10 Spray the tank contents through the boom. Drain any remainder from the tank.

Step 3

- 15 Rinse the interior tank surfaces with water; use about 10% of the tank capacity. Spray this rinse through the boom. Drain the remainder from the tank.

Step 4

- 20 Fill tank approximately half-full with fresh water and add the desired cleaning solution. Finish filling tank. Flush all lines and boom with cleaning solution (which can be water, or an ammonium hydroxide, or sodium hypochlorite solution) and agitate for 15 min. Spray 10 to 20 gallons of the wash through the boom. Drain the remaining tank contents.

Step 5

- 25 Remove all nozzles, nozzle screens, in-line filters or filters of any type and clean thoroughly in a bucket of water and cleaning agent. Remove any residues or deposits using a brush.

Step 6

- 30 Rinse the interior tank surfaces with fresh water; use about 10% of the tank capacity to remove all traces of the cleaning solution. Spray the rinse through the boom. Drain the remainder from the tank.

Step 7

- Fill tank half full and add ammonium hydroxide to give a concentration of 0.3% of ammonia. Finish filling the tank. Flush all lines and boom with the ammonium hydroxide solution, and let agitate for 15 min. Sample ammonia water wash in tank (sample used for bioassay test). Spray 10 to 20 gallons through the boom and then sample at a nozzle (sample used for bioassay test). Drain the remainder of the contents.
- 10 Rinse all remaining ammonium hydroxide solution from the tank with fresh water. Note: Samples were buffered to an appropriate pH to insure stability of the sulfonyleurea and then kept frozen prior to analyses.

15

TABLE II

Sprayer Cleanout Trials
Sulfonyleurea with no Tank Mix Partner

<u>Sulfonyleurea</u>	<u>Initial Sulfonyleurea Concentration in Tank Mix</u>	<u>Percent Injury¹</u>
Thifensulfuron methyl	550 ppm	28
	550 ppm	32
	550 ppm	17
Potassium Salt of Thifensulfuron methyl	550 ppm	0
	550 ppm	0
	550 ppm	18
Chlorsulfuron	275 ppm	50
	275 ppm	100
	275 ppm	100
Ammonium Salt of Chlorsulfuron	275 ppm	0
	275 ppm	0
	275 ppm	5
Metsulfuron methyl	275 ppm	85
	275 ppm	100
	275 ppm	30

14

Potassium Salt of	275 ppm	8
Metsulfuron methyl	275 ppm	0
Sodium Salt of	275 ppm	64
Metsulfuron methyl		

¹Percent injury to greenhouse sugarbeets after sprayed with final ammonia wash water from the tank cleanout procedure.

5

TANK CLEANOUT PROTOCOL II
(Sulfonylurea With No Tank Partner)

Step 1

Divide the sulfonylurea sample to be tested into 2 equal portions. Prepare a concentrated slurry with one portion, and a paste with the other portion. Spread and/or spray the paste and slurry onto the tank interior and let sit overnight. This procedure produces dried deposits on the tank surfaces to simulate worse-case field conditions.

15

Step 2

Rinse the tank interior with clean water, using a volume of 10-20% of the tank capacity, allowing the rinse to flush through the boom and hoses.

Step 3

Fill the tank with clean water and agitate for 10 minutes. Discard the water, flushing at least 10-20% through the boom and nozzles.

Step 4

Remove any nozzles, nozzle screens and in-line filters and clean with fresh water.

Step 5

Rinse the tank with clean water, using a volume of 10-20% of the tank capacity. Allow the rinse water to accumulate in the tank and then discard through the boom and nozzles. Drain any remaining rinse water from the tank.

Step 6

- Fill the tank half full with water and add ammonium hydroxide to give a concentration of 0.3% ammonia. Finish filling the tank. Flush all lines and boom with the ammonium hydroxide solution and let agitate for 15 minutes. Sample ammonia water wash in tank (sample used for bioassay test). Spray 10-20% through the boom and then sample at a nozzle (sample used for bioassay test). Drain the remainder of the tank contents.
- 10 Rinse all remaining ammonium hydroxide solution from the tank with fresh water. NOTE: Samples are buffered to an appropriate pH to insure stability of the sulfonylurea and then kept frozen prior to analyses.

BIOASSAY PROTOCOL

- 15 The bioassay protocol employed to determine the percent injury of the crop (sugarbeets) sprayed with the final rinse solution after tank cleanout of the ingredients listed in the Tables is as follows. Sugarbeet seedlings (at the two-leaf stage) were grown in the greenhouse (14 hour photoperiod at 21°C with light and 10 hours at 17°C in the dark) and sprayed with unmodified samples of effluent from various sprayer cleanout procedures. An automatic belt sprayer was used, and the samples were applied at a rate of approximately 45 gal/A. Three replicate pots, with four sugarbeet plants/pot, were treated with each sample. The sprayer was rinsed 12 times between each sample to ensure that there would not be carryover between samples.
- 30 Plants were held in the greenhouse until they were evaluated, 14 to 23 days after treatment. Injury of treated plants was assessed visually on a scale of 0 to 100 (0=no injury, 100=complete kill) compared to control plants. Injury ratings were based on the presence of various symptoms including reduced biomass,
- 35

stunting, inhibited development, chlorosis, necrosis, leaf spotting, and leaf puckering or deformation.

Formulation

Compounds of this invention will generally be used in formulation with an agriculturally suitable carrier comprising a liquid or solid diluent or an organic solvent. Use formulations include dusts, granules, pellets, solutions, Table B, suspensions, emulsions, gels, actives in plastic, wettable powders, emulsifiable concentrates, dry flowables and the like, consistent with the physical properties of the active ingredient, mode of application and environmental factors such as soil type, moisture and temperature. Sprayable formulations can be extended in suitable media and used at spray volumes from about one to several hundred liters per hectare. High strength compositions are primarily used as intermediates for further formulation. The formulations will typically contain effective amounts of salts of sulfonylurea(s), diluent and surfactant within the following approximate ranges which add up 100 weight percent.

	<u>Weight Percent</u>		
	<u>Active Ingredient</u>	<u>Diluent</u>	<u>Surfactant</u>
Wettable Powders	5-95	0-95	0-10
Oil Suspensions, Emulsions, Solutions, (including Emulsifiable Concentrates)	1-50	40-99	0-15
Pesticide Impregnated Film	1-80	20-99	0-15
Dusts	1-25	70-99	0-5
Granules	0.01-99	5-99.99	0-15
Water Dispersible Granules/Pellets	1-90	5-99	0-15

Tablets	10-60	40-99	0-5
High Strength Compositions	90-99	0-10	0-2
Gels	1-70	0-99	0-10

Typical solid diluents are described in Watkins, et al., *Handbook of Insecticide Dust Diluents and Carriers*, 2nd Ed., Dorland Books, Caldwell, New Jersey.

- 5 Typical liquid diluents and solvents are described in Marsden, *Solvents Guide*, 2nd Ed., Interscience, New York, 1950. *McCutcheon's Detergents and Emulsifiers Annual*, Allured Publ. Corp., Ridgewood, New Jersey, as well as Sisely and Wood, *Encyclopedia of Surface Active*
10 *Agents*, Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth, etc.

- Solutions are prepared by simply mixing the
15 ingredients. Fine solid compositions are made by blending and, usually, grinding as in a hammer mill or fluid energy mill. Water-dispersible granules can be produced by agglomerating a fine powder composition; see for example, Cross et al., *Pesticide Formulations*,
20 Washington, D.C., 1988, pp 251-259. Suspensions are prepared by wet-milling; see, for example, U.S. 3,060,084. Granules and pellets can be made by spraying the active material upon preformed granular carriers or by agglomeration techniques. See Browning,
25 "Agglomeration", *Chemical Engineering*, December 4, 1967, pp 147-48, *Perry's Chemical Engineer's Handbook*, 4th Ed., McGraw-Hill, New York, (1963), pages 8-57 and following, and WO 91/13546. Pellets can be prepared as described in U.S. 4,172,714. Water-dispersible and
30 water-soluble granules can also be prepared as taught in DE 3,246,493.

For further information regarding the art of formulation, see U.S. 3,235,361, Col. 6, line 16 through Col. 7, line 19 and Examples 10-41; U.S. 3,309,192, Col. 5, line 43 through Col. 7, line 62 and
 5 Examples 8, 12, 15, 39, 41, 52, 53, 58, 132, 138-140, 162-164, 166, 167 and 169-182; U.S. 2,891,855, Col. 3, line 66 through Col. 5, line 17 and Examples 1-4; Klingman, *Weed Control as a Science*, John Wiley and Sons, Inc., New York, (1961), pp 81-96; and Hance et
 10 al., *Weed Control Handbook*, 8th Ed., Blackwell Scientific Publications, Oxford, (1989).

In the following Examples, all percentages are by weight and all formulations are worked up in conventional ways. Compound 1 is the ammonium salt of
 15 chlorsulfuron.

Example A

High Strength Concentrate

	Compound 1	98.5%
	silica aerogel	0.5%
20	synthetic amorphous fine silica	1.0%.

Example B

Wettable Powder

	Compound 1	65.0%
	sodium alkyl naphthalenesulfonate	2.0%
25	sodium ligninsulfonate	4.0%
	sodium silicoaluminate	6.0%
	montmorillonite (calcined)	23.0%.

Example C

Granule

30	Compound 1	10.0%
	attapulgit granules (low volatile matter, 0.71/0.30 mm; U.S.S. No. 25-50 sieves)	90.0%.

Example DWater Dispersible Granule/Pellet

	Compound 1	25.0%
	anhydrous sodium sulfate	10.0%
5	crude calcium ligninsulfonate	5.0%
	sodium alkyl naphthalenesulfonate	1.0%
	calcium/magnesium bentonite	59.0%.

CLAIMS

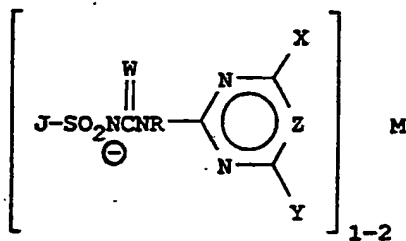
1. A method for reducing residual sulfonylurea pesticide contamination of a spray tank from which the sulfonylurea is applied, comprising the steps:

i) formulating the sulfonylurea as an agriculturally suitable water soluble salt composition before spray tank application, thereby increasing solubility of the sulfonylurea and decreasing the amount of insoluble sulfonylurea available for residual contamination of the spray tank,

ii) applying the sulfonylurea salt composition to the crop while minimizing buildup of insoluble sulfonylurea in the spray tank, and

iii) rinsing the spray tank substantially free of residual sulfonylurea, after application, in an operation in which the sulfonylurea remaining in the spray tank is reduced significantly versus the amount remaining when sulfonylurea is not formulated as a water-soluble salt before application.

2. A method according to Claim 1 employing, in step i, the following sulfonylurea salt:

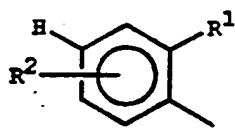
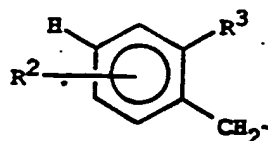
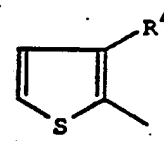
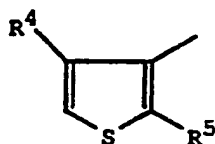
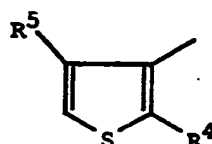
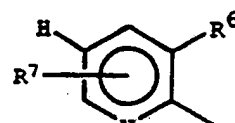
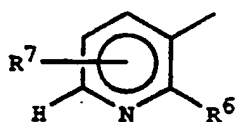
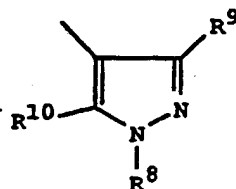
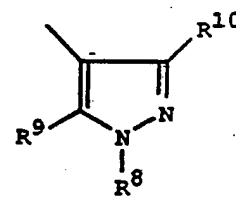
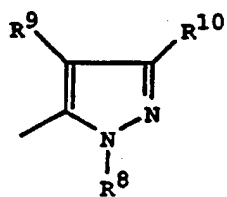
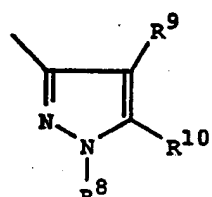
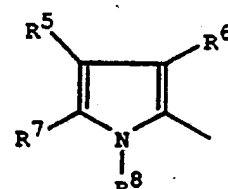
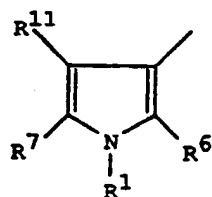


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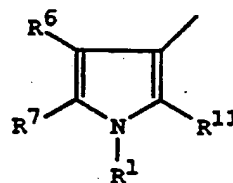
wherein:

J is selected from the group

21

J-1J-2J-3J-4J-5J-6J-7J-8J-9J-10J-11J-12J-13

and

J-14

R is selected from the group H and CH₃;

R¹ is selected from the group F, Cl, Br, NO₂, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₃-C₄ cycloalkyl, C₂-C₄ haloalkenyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy,

- C₂-C₄ alkoxyalkoxy, CO₂R¹², C(O)NR¹³R¹⁴,
SO₂NR¹⁵R¹⁶, S(O)_nR¹⁷, C(O)R¹⁸, CH₂CN and L;
R² is selected from the group H, F, Cl, Br, CN,
CH₃, OCH₃, SCH₃, CF₃ and OCF₂H;
5 R³ is selected from the group Cl, NO₂, CO₂CH₃,
CO₂CH₂CH₃, SO₂N(CH₃)₂, SO₂CH₃, SO₂CH₂CH₃, OCH₃,
and OCH₂CH₃
R⁴ is selected from the group C₁-C₃ alkyl, C₁-C₂
haloalkyl, C₁-C₂ alkoxy, C₂-C₄ haloalkenyl, F,
10 Cl, Br, NO₂, CO₂R¹², C(O)NR¹³R¹⁴, SO₂NR¹⁵R¹⁶,
S(O)_nR¹⁷, C(O)R¹⁸ and L;
R⁵ is selected from the group H, F, Cl, Br and CH₃;
R⁶ is selected from the group C₁-C₃ alkyl, C₁-C₂
alkoxy, C₂-C₄ haloalkenyl, F, Cl, Br, CO₂R¹²,
15 C(O)NR¹³R¹⁴, SO₂NR¹⁵R¹⁶, S(O)_nR¹⁷, C(O)R¹⁸ and L;
R⁷ is selected from the group H, F, Cl, CH₃ and
CF₃;
R⁸ is selected from the group H, C₁-C₃ alkyl and
pyridyl;
20 R⁹ is selected from the group C₁-C₃ alkyl, C₁-C₂
alkoxy, F, Cl, Br, NO₂, CO₂R¹², SO₂NR¹⁵R¹⁶,
S(O)_nR¹⁷, OCF₂H, C(O)R¹⁸, C₂-C₄ haloalkenyl and
L;
R¹⁰ is selected from the group H, Cl, F, Br, C₁-C₃
25 alkyl and C₁-C₂ alkoxy;
R¹¹ is selected from the group H, C₁-C₃ alkyl, C₁-C₂
alkoxy, C₂-C₄ haloalkenyl, F, Cl, Br, CO₂R¹²,
C(O)NR¹³R¹⁴, SO₂NR¹⁵R¹⁶, S(O)_nR¹⁷, C(O)R¹⁸ and L;
R¹² is selected from the group allyl and propargyl
30 and C₁-C₃ alkyl optionally substituted by at
least one member independently selected from
halogen, C₁-C₂ alkoxy and CN;
R¹³ is selected from the group H, C₁-C₃ alkyl and
C₁-C₂ alkoxy;
35 R¹⁴ is C₁-C₂ alkyl;

R¹⁵ is selected from the group H, C₁-C₃ alkyl, C₁-C₂ alkoxy, allyl and cyclopropyl;

R¹⁶ is selected from the group H and C₁-C₃ alkyl;

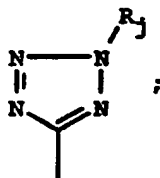
R¹⁷ is selected from the group C₁-C₃ alkyl, C₁-C₃ haloalkyl, allyl and propargyl;

R¹⁸ is selected from the group C₁-C₄ alkyl, C₁-C₄ haloalkyl and C₃-C₅ cycloalkyl optionally substituted by halogen;

n is 0, 1 or 2;

M is a cation;

L is



R_j is selected from the group H and C₁-C₃ alkyl;

W is selected from the group O and S;

X is selected from the group H, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, C₁-C₄ haloalkyl, C₁-C₄ haloalkylthio, C₁-C₄ alkylthio, halogen, C₂-C₅ alkoxyalkyl, C₂-C₅ alkoxyalkoxy, amino, C₁-C₃ alkylamino and di(C₁-C₃ alkyl)amino;

Y is selected from the group H, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, C₁-C₄ alkylthio, C₁-C₄ haloalkylthio, C₂-C₅ alkoxyalkyl, C₂-C₅ alkoxyalkoxy, amino, C₁-C₃ alkylamino, di(C₁-C₃ alkyl)amino, C₃-C₄ alkenyloxy, C₃-C₄ alkynyloxy, C₂-C₅ alkylthioalkyl, C₂-C₅ alkylsulfinylalkyl, C₂-C₅ alkylsulfonylalkyl, C₁-C₄ haloalkyl, C₂-C₄ alkynyl, C₃-C₅ cycloalkyl, azido and cyano;

Z is selected from the group CH and N;

provided that i) when one or both of X and Y is C₁ haloalkoxy, then Z is CH; and ii) when X is halogen, then Z is CH and Y is OCH₃, OCH₂CH₃, N(OCH₃)CH₃, NHCH₃, N(CH₃)₂ or OCF₂H.

- 5 3. A method according to Claim 2 employing a sulfonylurea salt of a sulfonylurea selected from the group: 2-chloro-N-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide (chlorsulfuron); methyl 2-[[[(4,6-dimethyl-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoate (sulfometuron methyl); ethyl 2-[[[(4-chloro-6-methoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoate (chlorimuron ethyl); methyl 2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoate (metsulfuron methyl); methyl 2-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-6-(trifluoromethyl)-3-pyridinecarboxylate; methyl 2-[[[(4-ethoxy-6-(methylamino)-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoate (ethametsulfuron methyl); 2-(2-chloroethoxy)-N-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide; ethyl 5-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-1-methyl-1H-pyrazole-4-carboxylate; N-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2-pyridinesulfonamide (rimsulfuron); methyl 3-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylate (thifensulfuron methyl); methyl 2-[[[N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-N-methylamino]carbonyl]amino]sulfonyl]benzoate (tribenuron methyl); methyl 2-[[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]methyl]benzoate (bensulfuron methyl); 2-[[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-N,N-dimethyl-3-pyridinecarboxamide (nicosulfuron);

methyl 2-[[[[[4,6-bis(difluoromethoxy)-2-pyrimidinyl]amino]carbonyl]amino]sulfonyl]benzoate; methyl 2-[[[[[4-dimethylamino)-6-(2,2,2-trifluoroethoxy)-1,3,5-triazin-2-

- 5 yl]amino]carbonyl]amino]sulfonyl]-3-methylbenzoate; and N-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-1-methyl-4-(2-methyl-2H-tetrazol-5-yl)-1H-pyrazole-5-sulfonamide.

4. A method according to Claim 3 employing a
10 salt of at least one member of the group methyl 3-[[[[[4-methoxy-6-methyl-1,3,5-triazin-2-yl]amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylate (thifensulfuron methyl), methyl 2-[[[[[4-methoxy-6-methyl-1,3,5-triazin-2-
15 yl]amino]carbonyl]amino]sulfonyl]benzoate (metsulfuron methyl), methyl 2-[[[N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-N-methylamino]carbonyl]amino]sulfonyl]-benzoate (tribenuron methyl) and 2-chloro-N-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-
20 yl]amino]carbonyl]benzenesulfonamide (chlorsulfuron) wherein M is selected from the group sodium, potassium, calcium, ammonium, and alkylammonium.

5. A method according to Claim 3 employing a sulfonylurea salt in the absence of a tank mix partner.

- 25 6. A method according to Claim 4 employing a sulfonylurea salt in the absence of a tank mix partner.

7. A method according to Claim 3 employing a sulfonylurea salt in the presence of a tank mix partner.

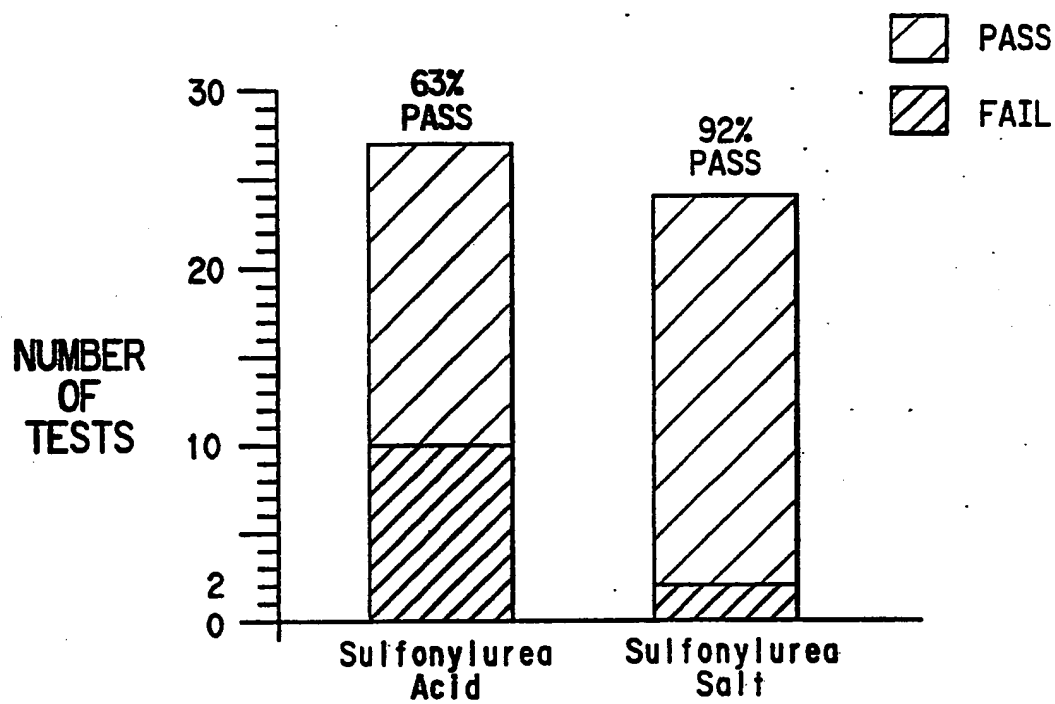
- 30 8. A method according to Claim 4 employing a sulfonylurea salt in the presence of a tank mix partner.

9. A method according to Claim 6 wherein spray tank cleanout is improved by a factor of at least 4.

10. A method according to Claim 8 wherein the spray tank cleanout is improved by a factor of at least 4.

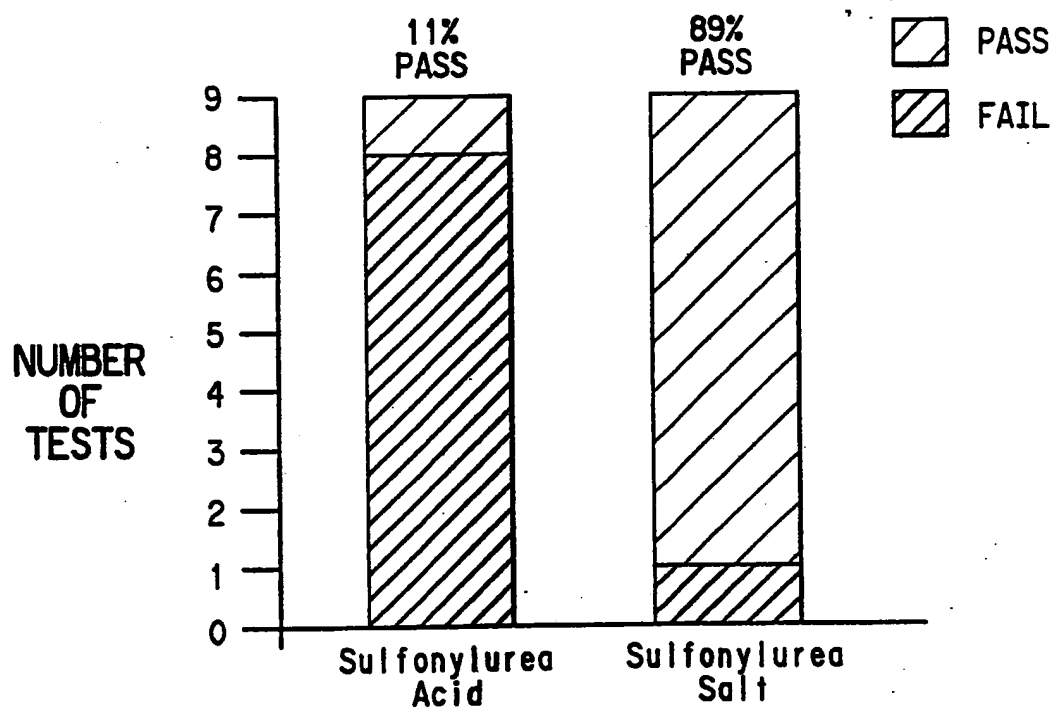
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FIG. 1



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FIG. 2



INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 93/01295

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 A01N47/36		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	A01N	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0 304 282 (DU PONT) 22 February 1989 see page 9, line 10 - line 14 see page 11, line 38 - line 39 see claims ---	1-10
X	EP,A,0 124 295 (DU PONT) 7 November 1984 see claims ---	1-10
X	US,A,4 599 412 (L.S. SANDELL) 8 July 1986 see claims see column 3, line 45 - line 58 -----	1-10
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
18 MAY 1993		10. 06. 93
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		DECORTE D.M.

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9301295
SA 70413

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0304282	22-02-89	AU-A- 2301988	09-03-89
		WO-A- 8901477	23-02-89
EP-A-0124295	07-11-84	AU-B- 558344	29-01-87
		CA-A- 1231246	12-01-88
		JP-B- 5008164	01-02-93
		JP-A- 59205305	20-11-84
		US-A- 4936900	26-06-90
		AU-A- 2631984	29-08-85
US-A-4599412	08-07-86	None	

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